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(54) Title: PRINTED WIRING BOARD(S) HAVING POLYIMIDEBENZOXAZOLE DIELECTRIC LAYER(S) AND THE MANUFACTURE THEREOF			
(57) Abstract			
A film of polyimidebenzoxazole (PIBO) having an electrically conductive layer adhered to at least one face thereto, wherein the PIBO film has a tensile strength greater than 200 MPa. A printed wiring board having at least one dielectric layer and at least one circuitry layer wherein at least one dielectric layer is a PIBO film. A printed wiring board (PWB) having at least one polyimidebenzoxazole (PIBO) dielectric layer wherein the PWB has at least one thin dielectric base material layer, at least one thin conductor, at least one narrow conductor width and at least one small diameter via.			

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PRINTED WIRING BOARD(S) HAVING POLYIMIDEBENZOXAZOLE  
DIELECTRIC LAYER(S) AND THE MANUFACTURE THEREOF

The present invention relates to printed wiring  
5 boards and the use of polymers as the base material in  
panels used to manufacture printed wiring boards.

A printed wiring board is typically made from at  
least one basic building block referred to in the industry  
as a panel. A panel is a sheet of specific size comprised  
10 of a conductive layer adhered to and completely covering one  
or both faces of a dielectric layer. Panels are commonly  
thin squares or rectangles having sides ranging in length  
from 300 to 700 millimeters and a thickness of less than 0.3  
millimeter. The uninterrupted conductive layer is commonly  
15 referred to as cladding or clad. The panel dielectric layer  
is typically called a base material layer. The cladding  
thickness commonly ranges between 17 to 50 microns. The  
base material layer thickness commonly ranges between 75 to  
150 microns. Epoxy impregnated woven glass mats (glass-  
20 epoxy) are generally used as the base material. Copper is  
generally used for the cladding.

A printed wiring board (PWB) is a sheet of specific  
shape and size in which electrical components can be mounted  
to create a functioning electronic device, such as a  
25 computer memory module. The PWB gives mechanical support to  
and electrically interconnects the mounted electrical  
components, such as capacitors, resistors and integrated  
circuit chips (ICs). The PWB can also provide the means to  
connect said components to electrical power, ground and a  
30 greater device such as a computer. A PWB having at least  
two ICs is called a multichip module (MCM).

There are three types of printed wiring boards  
(PWBs): single-sided, double-sided, and multilayered. The  
single-sided PWB has one dielectric base material layer and  
35 one circuitry layer. A circuitry layer is a conductive  
layer of a PWB containing one or more electrical circuits  
connecting the mounted components and/or providing  
connections to power and ground of a greater device such as

a computer. The double-sided PWB has one dielectric base material layer and two circuitry layers. A multilayered printed wiring board is a laminate of alternating dielectric layers and circuitry layers, wherein the dielectric layers 5 can be dielectric base material layers or dielectric adhesive layers. The dielectric adhesive layers generally are used to bond together the multiple layers used in fabricating a multilayer PWB. Before being laminated, the dielectric adhesive layers which are in the form of a film 10 are commonly called prepgs.

A circuitry layer is comprised of features called conductors which form the printed circuit [that is, electrical circuit(s)]. A conductor is an electrically conductive area on a printed wiring board circuitry layer. 15 Examples of a conductor include a line (analogous to a wire), a land (an area where electrical components such as ICs, capacitors, and resistors are connected to a PWB), a via (a metal plated hole interconnecting at least two circuitry layers) and an annular ring. An annular ring is 20 the conductor surrounding a via on a circuitry layer.

The circuitry layer features are also described by their dimensional characteristics. For example, conductor spacing is the nearest edge-to-edge distance between two adjacent conductor elements, pitch is the distance from the 25 center of one conductor line to the center of an adjacent line, and conductor width is the distance from one edge to the opposing edge of an individual conductor.

Generally, a PWB circuitry layer is created in the cladding of a panel by a photoresist/etching process. 30 Typically, a panel is cut into more than one single-sided or double-sided PWB. A dielectric layer having at least one PWB circuitry layer present on its surface will be hereinafter referred to as a processed panel, wherein the circuitry layer is not in a state to accept electrical 35 components but can be laminated with other processed panels in the production of multilayer PWBs. The typical steps to make a double-sided PWB from a copper clad panel using a photoresist/etching process is described by, Printed Circuit

Board Basics 2nd Ed., M. Flatt, Miller Freeman, San Francisco, 1992.

A typical multilayer printed wiring board is formed by laminating two processed panels having circuitry layers 5 on both sides. These processed panels are usually laminated together using a prepreg. In forming PWBs containing glass-epoxy base materials, the prepreg is usually a partially cured glass-epoxy film. The processed panels are further prepared for laminating by treating the circuitry layers 10 with a compound to facilitate the bonding of the circuitry layers to the prepreg. Alternating layers of the processed panels and prepgs are placed in a die. In addition to the processed panels and prepgs, it is common to have a prepreg and then a metal foil layer (typically copper) as 15 the bottom and top layers in the die. The prepgs, processed panels and metal foil are laminated by applying heat and pressure to the die. After laminating, the prepreg and foil create an outer cladding on the laminate. The laminate is then processed using the above double-sided PWB 20 process or analogous process to form multilayer PWBs.

As electronic devices, such as computers and cellular phones, decrease in size while computing speed and capacity continue to increase, printed wiring boards have had to increase in circuit density and decrease in volume. 25 PWB circuit density is described by and is proportional to the number of component connecting leads which can be attached to a square inch of PWB surface. Increasing PWB circuit density and decreasing volume have necessitated the use of thinner dielectric base material layers, thinner 30 cladding layers, closer conductor spacing, narrower conductor width, and smaller diameter via holes.

As the development of higher circuit density multichip modules (MCMs) proceeds, direct surface mount chip technology, such as tab lead frame, wire bond and flip chip 35 mounting is increasingly being used; chip being short for an IC chip. Because the chips are direct surface mounted and MCMs exhibit substantial thermal cycling in service, a wiring board-chip coefficient of thermal expansion (CTE)

mismatch can cause chip failure or chip to PWB interconnection failure. Thus, the CTE in the XY plane needs to approach that of the chips to avoid breakage of the chip and/or the connections between the board and chip 5 during operation. The XY plane is the same as the plane defined by a PWB circuitry and base material layer. This requires the base material layer to have an XY CTE close to that of a silicon based IC chip.

A critical aspect in creating a PWB is the degree of 10 conformity of circuit features, such as vias, to their intended position relative to other features of the PWB. The degree of conformity to an intended position is called registration. PWB defects arising from inadequate registration often occur during lamination. Poor 15 registration occurs during lamination due to permanent base material distortion and induced stresses. The induced stresses arise from a coefficient of thermal expansion (CTE) mismatch between the base material and circuitry layers. Therefore, it is advantageous to have a base material layer 20 having sufficient stiffness and strength to resist stress-induced registration deficiencies such as warping. It is also advantageous to have a base material which exhibits minimal permanent deformation such as shrinkage during the lamination process.

25 Commercially available dielectric base materials are beginning to limit further reductions of PWB size, increases of PWB circuit density, and increases of PWB high frequency signal propagation speed. Glass-epoxy base material layers exhibit periodic roughness associated with a reinforcing 30 woven glass mat. This roughness limits how thin the base material and cladding can be which ultimately determines how thin the circuitry can be. In addition, a glass-epoxy layer typically has a linear coefficient of thermal expansion (CTE) between 12 to 17 parts per million (ppm)/°C in the XY 35 plane whereas an IC made out of silicon has a CTE on the order of 3 ppm/°C. This mismatch can cause chip or chip to PWB interconnection failure. Glass-epoxy base materials have a high dielectric constant of 4.5. This high

dielectric constant significantly slows signal propagation of high frequency circuits. In addition, due to the glass reinforcement, a glass-epoxy base material causes faster drill bit wear than a polymeric base material.

5 More recent base materials have attempted to address some of the problems associated with glass-epoxy base materials. For example, fiber reinforced (Kevlar and graphite reinforced) polyimide base materials have been developed. However, these materials have several 10 disadvantages such as high moisture absorption, high cost, high dielectric constant ( $>3$ ), and Kevlar has shown inferior adhesion to copper cladding.

Filled polytetrafluoroethylene (PTFE) has also been used to address limitations of a glass-epoxy base material 15 (for example, high dielectric constant). Fillers are required in PTFE because of its low inherent stiffness. PTFE fillers tend to cause the same problems glass reinforcement causes in glass-epoxy base material layers. PTFE base materials also display large lateral deformation 20 in the XY plane with respect to temperature. PTFE's large lateral deformation limits the registration attainable in a multilayer PWB.

Liquid crystal polymer (LCP) base materials have recently been developed. LCPs typically are stiff strong 25 polymers often having a dielectric constant less than 3. However, LCPs tend to lack good adhesion to metal cladding. Also, LCPs generally exhibit anisotropic coefficients of thermal expansion (CTE). In particular, LCPs tend to exhibit Z direction CTE significantly higher than the CTE of 30 copper. The Z direction is perpendicular to the XY plane. Due to thermal cycling during MCM operation, the copper-LCP CTE mismatch causes stress and can fracture a via's copper plating. As the via diameter decreases, the via copper 35 plating stress will be increased by the inverse square of the via diameter. Consequently, it will be difficult to make reliable small diameter vias in a multilayer PWB having LCP base material layers.

Therefore, it is desirable to furnish a panel capable of being formed into a single-sided, double-sided or multilayered PWB which can have high circuit density and fast high frequency signal propagation. Consequently, the 5 PWB, and in particular the multilayer PWB of this invention can be made having thin base material layers, thin circuitry layers, narrow conductor widths, close conductor spacings and small diameter vias.

An aspect of this invention is a film of 10 polyimidebenzoxazole (PIBO) having an electrically conductive layer adhered to at least one face thereto, wherein the PIBO film has a tensile strength greater than 200 MPa at 25°C. The tensile strength is determined by ASTM D-638-87B. The PIBO film having an electrically conductive 15 layer bonded thereto can be a panel, sheet, or processed panel.

Another aspect of this invention is a printed wiring board having at least one dielectric layer and at least one circuitry layer wherein at least one dielectric layer is a 20 PIBO film having a tensile strength greater than 200 MPa at 25°C as determined by ASTM D-638-87B. The previous aspect of this invention can be used to make said PWB.

With this invention, it is possible to fabricate a PWB having a thinner dielectric base material layer, a 25 thinner conductor, a closer conductor spacing, a narrower conductor width and a smaller diameter via, compared to glass-epoxy technology. Consequently, using this invention one may fabricate small, high circuit density, fast signal propagating MCMs which can meet the expected size reductions 30 and computing requirements of present and future electronic devices.

In the first aspect of this invention, the PIBO film adhered to one or two electrically conductive layers can be, for example, long sheets, panels or processed panels. The 35 long sheets may be rolled. To minimize slicing, the width of the cladded PIBO sheet is preferably the same width as a specified panel.

The electrically conductive layer can be any electrically conductive metal. Preferably the metal is copper, aluminum or alloys thereof.

5 The electrically conductive layer is preferably less than 50 microns and more preferably less than 17 microns thick.

It is advantageous to have a thin base material bonded to a thin cladding or a thin circuitry layer to create a small high circuit density PWB. PIBO films as thin 10 as 0.1 micron and as thick as 2000 microns can be used. The preferred thickness of the PIBO film used as a base material layer is less than 125 microns and the most preferred is a thickness less than 50 microns. Because of PIBO stiffness, high strength, and surface smoothness, a thin base material 15 layer of 25 microns or less is possible. However, it is preferred that the PIBO film have a thickness of at least 5 microns.

The PIBO film may have a filler such as glass fibers and ceramic particulates. However, it is preferred to use 20 the PIBO film without fillers. Base material layers without filler typically have smoother surfaces compared to base material layers having filler. Smoother surfaces enable thinner circuitry layers.

Any PIBO polymer may be a film and function as a PWB 25 dielectric layer. It is preferred the PIBO have at least one of these physical properties: high stiffness, high strength, low dielectric constant, XY plane CTE approaching the CTE of silicon, Z plane CTE of less than 100 ppm/°C and low permanent deformation upon heating to 300°C. A filler 30 may be used to achieve one or more of the preferred properties, but it is preferred a PIBO film without filler meet the preferred property limitations.

Polyimidebenzoxazole is typically made by imidizing a polyamic acid which is the reaction product of a 35 dianhydride monomer and a dianaminobenzoxazole monomer.

Imidization is the condensation reaction of the amic acid linkages of the polyamic acid, which consequently forms the imide linkages of the polyimidebenzoxazole. In copending

applications, Serial No. 331,775, filed October 31, 1994, for "Polyamic Acids and Methods to Convert Polyamic Acids into Polyimidebenzoxazole Films" and "Polymeric Acid Precursors and Methods For Preparing Higher Molecular Weight 5 Polyamic Acids and Polyimidebenzoxazole," filed April 24, 1995 (Serial No. not available), procedures and reactants to form PIBO films are described and are incorporated by reference. Preferred polyamic acids, in which a PIBO film is prepared therefrom, are the reaction products of:

10 pyromellitic dianhydride and 5-amino-2-(p-aminophenyl)benzoxazole, pyromellitic dianhydride and 2,6-(4,4'-diaminodiphenyl) benzo[1,2-d:5,4-d'] bisoxazole, and pyromellitic dianhydride and 2,2'-p-phenylene-bis(5-aminobenzoxazole).

15 Because it is beneficial to have a stiffer and stronger base material layer, particularly for a rigid PWB, a PIBO film exhibiting an elastic modulus of 0.5 GPa or greater is preferred. A tensile strength of 250 MPa or greater, as determined by ASTM D-638-87B, is also preferred. 20 A PIBO film having an elastic modulus of greater than 5 GPa is more preferable. A PIBO film having a tensile strength greater than 300 MPa is also more preferable.

To minimize failures of surface mounted IC chips, it is preferred the PIBO film used as a base material layer 25 have an XY plane linear CTE between 1 and 7 ppm/°C from -55°C to 125°C. It is preferred that the PIBO film have a Z direction CTE of less than 100 ppm/°C from -55°C to 125°C.

To allow faster signal propagation at higher frequencies, it is preferred the PIBO film have a dielectric 30 constant between 2 and 3.3 from 1 MHz to 1 GHz. The PIBO film dissipation factor is preferred to be at most 0.01 as determined by test IPC 650 2.5.8A.

To minimize registration problems, PIBO film having a permanent lateral deformation of less than 0.02 percent 35 determined by IPC 650 2.2.4A is also preferred.

To make the first aspect of this invention a PIBO film must be formed. Typically, to make a PIBO film, a polyamic acid is made by reacting a dianhydride monomer and

a diaminobenzoxazole monomer in a solvent. The resultant polyamic acid is typically soluble in the solvent. The polyamic acid/solvent will be referred to as the polyamic acid solution. The polyamic acid solution or a PIBO 5 solution formed by imidizing the polyamic acid in solution is then shaped into a film. When the polyamic acid solution is made into a film, it is subsequently imidized to form the PIBO film. The PIBO film may then be heat treated to remove any remaining solvent or enhance certain film properties.

10       Typically, the dianhydride monomer and diaminobenzoxazole monomer are reacted in a solvent. The solvent typically is a polar, aprotic solvent such as N,N-dimethylacetamide, N-methylpyrrolidinone, 1,3-dimethyl-5-imidazolidinone, N,N-dimethylformamide, 1,1,3,3-tetramethylurea, or N-cyclohexylpyrrolidinone. Mixtures of 15 one or more polar aprotic liquids may also be employed as the solvent. Before shaping of a polyamic acid solution, portions of said solvent can be removed by the application of heat; extracting said solvent using a solvent which is a 20 non-solvent for the polyamic acid; or a combination of both. The temperature to remove the solvent is preferably less than a temperature which will cause imidization of the polyamic acid. The polyamic acid typically binds some of the solvent until imidization, thereby making it difficult 25 to reduce the solvent level by volatilization to below 10 weight percent.

When the polyamic acid PIBO imidization product is insoluble in the solvent of the polyamic acid solution, the polyamic acid solution prior to imidization is preferably 30 formed into a film. An unsupported film may be formed using a technique involving shear such as extrusion. Shaping the polyamic acid solution to form a film can also be done by coating, casting, dipping or spraying the polyamic solution onto an appropriate substrate. An appropriate substrate 35 includes glass, aluminum, stainless steel, silicon, copper, polyimide film, tetrafluoroethylene fluorocarbon polymers (marketed as Teflon™). Often a release agent such as a

fluorinated polymer or a silicone oil can be used to facilitate removal of the film from the substrate.

When the polyamic acid PIBO imidization product is soluble in the polyamic acid solution solvent, it is not 5 normally necessary and may not be desirable to form the polyamic acid solution into a film. Thus, the polyamic acid in the polyamic acid solution is first imidized and subsequently formed into a film as described in the previous paragraph.

10 Regardless of the forming method, imidization of the polyamic acid to PIBO may be carried out by heating or employing a catalyst or combinations thereof. The polyamic acid can be imidized to PIBO by heating the polyamic solution or the polyamic acid solution after removal of some 15 of the solvent. Catalyzing agents can be added to the polyamic acid solution or the polyamic acid solution after removal of some of the solvent. Catalysts which can be employed include dehydration agents such as acetic anhydride, propionic anhydride, ketene and isobutyric 20 dianhydride. While these catalysts can be employed alone they are most preferably employed with an organic base, preferably those which do not form inorganic salts. Examples include picoline, pyridine, isoquinoline, triethylamine, lutidine or their mixtures. The application 25 of heat or addition of catalysts may occur before or after a film has been formed.

In this invention, the use of heat is preferred to imidize the polyamic acid to PIBO. In particular and surprisingly, a heating process resulting in PIBO films with 30 enhanced tensile strength and percent elongation is more preferably used. In general, the process involves the following heating steps. First, the film is imidized at a temperature from 185°C to 280°C, more preferably from 185°C to 240°C and most preferably 230°C, for a time of at least 5 35 minutes and no more than 90 minutes, more preferably from 10 to 80 minutes and most preferably from 15 to 75 minutes in air or an inert atmosphere that is preferably moisture free. Subsequently, the imidized film is preferably further heat

treated to improve the PIBO properties by heating the film from 250°C, preferably from 300°C to a temperature which is less than 600°C and less than the glass transition temperature of the resultant PIBO for at least 10 seconds.

5 More preferably the further heat treatment is performed at a lower temperature from 250°C to 350°C in air or an inert atmosphere, and then at a second higher temperature from 350°C to 500°C in air or an inert atmosphere. The inert atmosphere is most preferably nitrogen.

10 After a PIBO film has been made, an electrically conductive layer must be adhered to said PIBO film forming, for example, a sheet, panel or processed panel. The PIBO film having an adhered electrically conductive layer can then be fabricated into a PWB.

15 An electrically conductive layer can be adhered to a PIBO film by directly forming a polyamic acid film on an electrically conductive foil and subsequently imidizing the polyamic acid solution to form a PIBO film. Preferably the foil is copper, aluminum or alloys thereof. The foil then 20 functions as the electrically conductive layer of the PIBO film of this invention. The adhesion of the PIBO film to the foil can be enhanced by use of an adhesion promoter such as 3-aminopropyltriethoxysilane.

An electrically conductive layer can also be applied 25 to a PIBO film by techniques such as vapor deposition, electroless plating, electroplating, sputtering and combinations thereof. Vapor deposition, sputtering, and electroplating are described in Electronic Packaging and Production, May, 1992, pages 74-76. Vapor deposition, 30 sputtering, electroplating, and electroless plating are described in more detail in Handbook of Tribology Materials, Coatings, and Surface Treatments, B. Bhushan & B.K. Gupta, Chapters 9-10, McGraw-Hill, Inc., 1991.

Often a seed metal/metal oxide layer(s) may be 35 applied to the PIBO film to enhance adhesion of subsequent deposited layers. Examples of seed metal/metal oxides include nickel, chrome, titanium, chromium, iron, molybdenum or zirconium and is applied first to enhance adhesion of

subsequent metal deposits such as copper. The seed layer can be applied by several techniques such as electroless plating, sputtering and vapor deposition. The PIBO film surface can also be treated chemically, plasma or ion 5 treated to enhance the adhesion of the electrically conductive layer or seed layer to the PIBO surface.

In vapor deposition, material is evaporated under vacuum by a heat source such as resistance heating, LASER, and plasma, then the material is condensed on the PIBO film. 10 The technique is relatively fast but is preferably limited to a layer thickness of up to 0.2 micron. A thicker layer can be deposited by electroplating or electroless plating over the vapor deposited layer. The PIBO film adhesion can be enhanced by the same treatments previously described.

15 Sputtering involves putting the PIBO film in a vacuum chamber in which a material to be deposited functions as a cathode in a vacuum tube. The cathode is bombarded by ions from a gas and the subsequent liberated material ions are deposited on the PIBO. This deposition method typically 20 results in coatings of 500 nanometers or less on the PIBO film. A thicker electrically conductive layer can be deposited by electroless plating over the deposited layer. Again the PIBO surface can be pretreated as described previously.

25 In electroplating a metal film on the PIBO film, the process typically begins with a surface treatment such as a chemical, plasma and ion pretreatment of the PIBO film, followed by deposition of a thin seed metal/metal oxide barrier by techniques which include those described 30 hereinbefore. Metal is then continuously electroplated onto the seed metal layer to the desired thickness. Typically, the metal is plated from an aqueous solution of a salt containing ions of the element (metal) being deposited by passing an electric current through said solution, wherein 35 the PIBO acts as the cathode and the anode is the metal being deposited. The metal can be continuously electroplated by unrolling a long roll of PIBO film and passing said film sequentially through the aqueous solution.

An electroless plating process (chemical reduction deposition) may be used to adhere an electrically conductive layer to the PIBO film. The PIBO can be pretreated as described in the preceding paragraph. The electrically 5 conductive layer, preferably being copper, is plated onto the PIBO from a bath which is typically aqueous. The bath typically contains: a metal salt; a reducing agent; complexing agents; buffering agents; accelerators and inhibitors. The metal salt is the source of the metal. The 10 reducing agent supplies electrons for the reduction of metal ions produced by dissolving metal salts in water. Complexing agents control the free metal available to the reaction. Buffering agents maintain pH of the bath during the process. Accelerators help increase the speed of the 15 reaction. Inhibitors help control the reduction reaction. Heat is also commonly applied to facilitate the deposition process. Commonly, copper sulfate (CuSO<sub>4</sub>) is used as the salt and formaldehyde is used as the reducing agent.

Another method which may be used to adhere an 20 electrically conductive layer, preferably copper, aluminum or alloys thereof to the PIBO film, is to bond a foil of said metals to the PIBO film using an adhesive. Suitable adhesives include epoxy, cyanate ester, polyimide, and polyamic acid. The adhesive can be in the form of a liquid, 25 powder or a film. The adhesive can be applied to the metal foil, PIBO film or both. The adhesive can be applied by casting, dipping, spraying or pressing. The PIBO and metal foil can be adhered together by laminating said foil and film by applying heat and pressure.

30 After the PIBO film has been adhered to an electrically conductive layer, the PIBO film and adhered layer can be sliced into a specific size creating, for example, a panel or a processed panel. Slicing can be accomplished by methods such as laser cutting, mechanical 35 sawing and waterjet cutting.

A PWB having at least one PIBO dielectric layer can be a single-sided, double-sided or a multilayer PWB. For a single-sided and double-sided PWB, the PWB has a PIBO

dielectric layer and one or two circuitry layers, respectively, wherein the circuitry layer(s) provide the means for component mounting and/or interconnection, connection to external devices, power, and/or ground. The 5 PIBO dielectric layer provides the means for electrical insulation between circuitry layers and/or circuitry layer features while also providing mechanical support for the PWB.

The PWB of this invention can be rigid or flexible. 10 Generally a multilayer PWB having a PIBO dielectric layer will be substantially rigid. Single-sided and double-sided PWB having a PIBO dielectric layer may be flexible.

Because the PWB of this invention contains a PIBO dielectric layer, it is possible for the circuitry layer to 15 be less than 50 microns thick and more preferably less than 17 microns. For the same reason, this invention advantageously allows the circuitry layer to have one or more desirable circuitry features such as at least one conductor line width of less than 100 microns, at least one 20 conductor spacing of less than 100 microns, at least one annular hole ring width between 200 microns to a landless annular hole ring (0 microns) and at least one via diameter less than 200 microns. Said circuitry layer and/or features are preferably adhered to said PIBO layer.

25 Preferably the circuitry layer is copper, aluminum or alloys thereof.

The single or double-sided PWB of this invention may be formed by any convenient process. For example, said single or double-sided PWB may be fabricated by the 30 photoresist/etching process as described previously for a double-sided PWB which can also be used with little modification to form a single-sided PWB if desired. The single or double-sided PWB of this invention is not limited by any particular method to produce said single or double- 35 sided PWB.

In a multilayer PWB of this invention, the PWB consists of multiple alternating dielectric layers and circuitry layers which are connected by at least one via.

The simplest multilayer PWB has three circuitry layers and two dielectric base material layers. PWBs with ever increasing number of layers are becoming more common and may be advantageously achieved by this invention.

5        In the multilayer PWB of this invention, circuitry layers comprising the outer faces of the PWB typically provide places to mount electronic components such as IC chips, resistors and capacitors and electrically connect said components. The circuitry layer(s) in the interior of  
10 the PWB typically provides electrical connections between the mounted components, external devices, power and ground. The base material layer(s) typically provides rigidity (mechanical support) to the PWB, electrical insulation between circuitry layers and electrical insulation between  
15 conductors of a circuitry layer. The dielectric adhesive layer(s) typically provides bonding between circuitry layers, electrical insulation between circuitry layers and electrical insulation between conductors of a circuitry layer.

20        Because PIBO is not a thermoset or thermo-plastic polymer, it generally will not be used as an adhesive dielectric layer. Thus, in the multilayer PWB of this invention, the PIBO will typically be a base material layer and some other material will be the adhesive dielectric  
25 layer. However, a polyamic acid which forms a PIBO upon imidization may be used as an adhesive during the production of a multilayer PWB, consequently forming a PIBO adhesive dielectric layer. A PIBO film that has been coated with an adhesive may also be used to laminate layers together in a  
30 multilayer PWB process, subsequently forming a PIBO dielectric adhesive layer. The dielectric adhesive layer may be any material displaying good adhesion to the circuitry layer and PIBO after lamination. Preferably, the adhesive dielectric layer has a dielectric constant  
35 approaching the dielectric constant of the PIBO layer and is preferably less than 4.5. A dielectric adhesive layer derived from an adhesive such as epoxy, cyanate ester, and polyimide may be used. Said adhesive layers may have a

filler such as ceramic particulates or fibers. Preferably two PIBO processed panels can be adhesively bonded by an adhesive layer less than 130 microns and more preferably less than 50 microns thick.

5 The PWB of this invention desirably survives IPC 650 2.6.6B test, which describes reliability of a PWB thermal cycled between -55 to 125°C.

The multilayer printed wiring board of this invention may be formed by a process involving laminating 10 two or more processed panels having circuitry layers on both sides, wherein at least one of the processed panels has a PIBO base material layer. The processed panels are usually laminated together using an adhesive described previously. The adhesive may be a dry powder, a liquid, a film or a 15 paste. Preferably the adhesive is in the form of a film (prepreg). The PIBO processed panel can be treated to enhance adhesion of an adhesive layer. Treatments can include hand cleaning using pumice, plasma, chemical or coating treatments. Alternating layers of the processed 20 panels and preps are placed in a die. In addition to the processed panels and preps, it is common to have a prep and then a metal foil layer (typically copper) as the bottom and top layers in the die. The preps, processed panels and metal foil are laminated by applying 25 heat and pressure to the die. After laminating, the prep and foil create an outer cladding on the laminate. The laminate is then processed by any convenient method to create the outer circuitry layers which are ready to mount electronic components. The creation of the outer layers may 30 include drilling of vias which can be accomplished by techniques such as mechanical drilling, LASER drilling, or plasma ablation. Finally, if the laminated processed panels contain more than one multilayer PWB, the PWBs may be finished by slicing the laminated processed panels by 35 techniques previously described for slicing processed panels.

A preferred embodiment of this invention is a PWB having at least one dielectric layer which is PIBO, wherein

the PWB has a circuit density of at least 160 leads per square inch. Another most preferred embodiment is an MCM having surface mounted electronic components (ICs), wherein the PWB has at least one PIBO dielectric layer and the 5 circuit density of said PWB is greater than 160 leads per square inch.

Where examples of the invention are described hereinafter, it is intended that these examples illustrate rather than limit the general nature of the invention.

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#### EXAMPLES

##### Forming a PIBO Film and Adhering an Electrically Conductive Layer to the PIBO Film

###### Example 1A

15 Into a 3 neck, 25-mL round-bottom flask equipped with agitation means and a Dean-Stark trap with a condenser was fed 230 mL of N-methylpyrrolidinone (NMP) and 40 mL of toluene. The flask was gently purged by nitrogen. Toluene was distilled off. Into the stirred room temperature solvent was added 12.976 g of 5-amino-2-(p-aminophenyl)benzoxazole (pDAMBO) and 12.565 g of 20 pyromellitic dianhydride (PMDA) rinsed with 10.0 mL dry DMAc. After 68 hours at room temperature, the resulting polyamic acid was diluted with N-methylpyrrolidinone (NMP) and has an inherent viscosity of 3.73 g/dL.

25 To a dry, 3 neck, 250 mL round-bottom flask having a nitrogen atmosphere and equipped with agitation means and inlet and outlet adaptors was added 80 grams of the above polyamic acid solution. 12.1 mL of a dry mixture of 60 percent 1,3-dimethyl-imidazolidinone and 40 volume percent N-methylpyrrolidinone (DMI/NMP) was added to the flask and 30 stirred overnight at room temperature. The flask was chilled by an ice bath and degassed by aspirator vacuum. The flask was brought back to atmospheric pressure with nitrogen.

35 A 12.5 weight percent solution of the resulting polyamic acid was cast on glass as a 25 micron film. The film was heated in an air circulating oven at 60°C for 45 minutes, removed from the glass and secured in an aluminum

frame. It was then placed in an air-circulating oven, heated for 20 minutes at 225°C, for 20 minutes to 300°C, maintained for 1 hour at 300°C, then cooled to room temperature; and in a nitrogen atmosphere, heated for 27 minutes at 30°C (nitrogen purge cycle), 75 minutes to 400°C, maintained at 400°C for 12 hours, and then cooled to room temperature.

5 The above procedure was repeated to produce a 51 micron film.

10 The film's tensile strength was 308 MPa, its tensile modulus was 11 GPa, and its elongation at break was 8.5 percent.

Example 1B

15 The following procedure was used to make a PIBO film having one face clad by a 9 micron thick copper cladding. A 25 micron PIBO film made by the procedure of Example 1A was chemically treated for 45 to 75 seconds in a homogeneous aqueous solution having 45 weight percent potassium hydroxide, 10 weight percent ethylene diamine, and 10 weight 20 percent ethylene glycol. This process reduces the film thickness by 10 percent and makes the film surface more easily wetted so as to enhance adhesion of subsequent deposited layers. A nickel seed layer several microns thick was applied to the chemically treated PIBO film. The nickel 25 was applied by electroless plating. After the nickel seed layer was applied, a copper layer was deposited by electroplating in an acid copper sulfate bath at 30 amps per square foot for 45 minutes per 0.5 ounce per square foot of plating over the nickel seed layer.

30 The procedure of Example 1B was repeated to make a 25 microns thick PIBO film cladded by 17 microns thick copper on one face. The procedure of Example 1B was repeated to make a 25 microns thick PIBO film cladded by 35 microns thick copper on one face. The procedure of Example 35 1B was repeated to make a 51 microns thick PIBO film cladded by 9 microns thick copper on one face. The procedure of Example 1B was repeated to make a 51 microns thick PIBO film cladded by 17 microns thick copper on one face. The

procedure of Example 1B was repeated to make a 51 microns thick PIBO film cladded by 35 microns thick copper on one face.

The procedure of Example 1B was repeated to make a 5 25 microns thick PIBO film cladded by 9 microns thick copper on both faces. The procedure of Example 1B was repeated to make a 25 microns thick PIBO film cladded by 17 microns thick copper on both faces. The procedure of Example 1B was repeated to make a 25 microns thick PIBO film cladded by 35 10 microns thick copper on both faces. The procedure of Example 1B was repeated to make a 51 microns thick PIBO film cladded by 9 microns thick copper on both faces. The procedure of Example 1B was repeated to make a 51 microns thick PIBO film cladded by 17 microns thick copper on both 15 faces. The procedure of Example 1B was repeated to make a 51 microns thick PIBO film cladded by 35 microns thick copper on both faces.

#### Example 1C

The following procedure was used to make a PIBO film 20 having one face clad by a 9 micron thick copper cladding. To enhance adhesion of subsequent deposited layers, the PIBO film of Example 1A was treated using a plasma generated by an MRC 603 sputtering system using an argon or argon/oxygen gas flow of 75 standard cubic centimeters/minute (SCCM) at 25 75 to 125 millitorr pressure for 5 to 30 minutes at an RF power of 500 watts. A seed layer of copper 1000 Angstroms thick was sputter deposited onto the plasma treated PIBO film. A thicker layer of copper (9 microns) was deposited over the sputtered copper layer by electroplating in a 30 standard acid copper sulfate bath at 30 amps per square foot for 45 minutes per 0.5 ounce per square foot of plating.

The procedure of Example 1C was repeated to make a 25 microns thick PIBO film cladded by 17 microns thick copper on one face. The procedure of Example 1C was 35 repeated to make a 25 microns thick PIBO film cladded by 35 microns thick copper on one face. The procedure of Example 1C was repeated to make a 51 microns thick PIBO film cladded by 9 microns thick copper on one face. The procedure of

Example 1C was repeated to make a 51 microns thick PIBO film cladded by 17 microns thick copper on one face. The procedure of Example 1C was repeated to make a 51 microns thick PIBO film cladded by 35 microns thick copper on one face.

The procedure of Example 1C was repeated to make a 25 microns thick PIBO film cladded by 9 microns thick copper on both faces. The procedure of Example 1C was repeated to make a 25 microns thick PIBO film cladded by 17 microns thick copper on both faces. The procedure of Example 1C was repeated to make a 25 microns thick PIBO film cladded by 35 microns thick copper on both faces. The procedure of Example 1C was repeated to make a 51 microns thick PIBO film cladded by 9 microns thick copper on both faces. The procedure of Example 1C was repeated to make a 51 microns thick PIBO film cladded by 17 microns thick copper on both faces. The procedure of Example 1C was repeated to make a 51 microns thick PIBO film cladded by 35 microns thick copper on both faces.

All of the claddings of the above examples passed IPC-TM-650, Method 2.4.9 adhesion test.

#### Formation of a PIBO Multilayer PWB

##### Example 2

A 63.5 mm x 48 mm x 0.18 mm multilayer PWB having 4 circuitry layers and 3 dielectric layers was made in which the dielectric layers were PIBO. The multilayer PWB includes: 76 microns wide conductors; 76 microns wide conductor spacings; 152 microns pitch and via hole diameters of 203, 305, and 508 microns.

The PWB was created by the following procedure. The cladding of two 9 microns thick copper single-faced cladded 25 microns thick PIBO films of Example 1B were coated with Dupont Riston 9015™ photoresist, masked by an artwork photo tool and exposed to UV light. The resist was developed in a 2 weight percent sodium carbonate aqueous solution. The copper not protected by the photoresist was etched away by a sulfuric-peroxide solution. The remaining photoresist was etched away using a caustic solution and then the surfaces

were further cleaned by hand using pumice. Each PIBO film now has one face having a circuitry layer (PIBO-circuitry film).

The 2 PIBO-circuitry films, 2 copper foils and 3 plasma etched PIBO films in which each face has been joined to an epoxy adhesive film (PIBO epoxy adhesive film) were placed in a lamination fixture. The layers were stacked in the lamination fixture as follows: (1st layer) copper foil; (2nd layer) PIBO epoxy adhesive film; (3rd layer) PIBO-circuitry film; (4th layer) PIBO epoxy film; (5th layer) PIBO-circuitry film; (6th layer) PIBO epoxy adhesive film and (7th layer) copper foil. The circuitry layers of the PIBO-circuitry films were facing the 4th layer in the stack. The fixture and stack were placed in an elastomeric bag which was evacuated. The stack was laminated by placing the evacuated bag in a preheated press and pressing at 400 psi at 340°F for one hour.

Holes were drilled in the laminate using a drill rotating at 110,000 rpm. Hole diameters of 203, 305 and 508 microns were drilled. For the 305 and 508 microns holes, the laminate was covered with an aluminum/phenolic material to minimize damage to the laminate upon drill entry. The drilled holes were then plasma etched to remove debris and desmear the epoxy adhesive. Vias were created by electroless plating copper in the holes followed by electroplating copper to a thickness of 2.5 microns.

The outer copper layer was coated with the Dupont photoresist, masked with another photo tool and exposed to UV light. The photoresist was developed using 2 weight percent sodium carbonate aqueous solution leaving areas of exposed copper. The exposed copper was plated with 3 microns of copper by electroplating which was then overlaid by etch resist consisting of 2.5 microns of nickel and then 0.25 micron of gold deposited by an electroplating process. The copper having photoresist was removed by a sulfur-peroxide etchant. The copper coated with etch resist remains making up the outer circuitry layer. To the outer circuitry layers, a solder mask was added to protect the

outer circuitry features which will not be used to mount electronic components such as lines

The same multilayer PWB was formed by procedure of Example 2 and was repeated for two 9 microns thick copper 5 single-faced cladded 25 microns thick PIBO films of Example 1C.

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## WHAT IS CLAIMED IS:

1. A polyimidebenzoxazole (PIBO) film having an electrically conductive layer adhered to at least one face thereto wherein the PIBO film has a tensile strength greater than 200 MPa at 25°C.
2. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the PIBO film is less than 150 microns thick.
3. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the PIBO film is less than 50 microns thick.
- 10 4. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the electrically conductive layer is less than 50 microns thick.
- 15 5. The polyimidebenzoxazole (PIBO) film of Claim 4 wherein the electrically conductive layer is less than 17 microns thick.
6. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the electrically conductive layer is selected from the group consisting of copper, aluminum or alloys thereof.
- 20 7. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the polyimidebenzoxazole (PIBO) film is selected from the group consisting of:
  - a) the reaction product of pyromellitic dianhydride and 5-amino-2-(p-aminophenyl) benzoxazole;
  - b) the reaction product of pyromellitic dianhydride and 2,6-(4,4'-diaminodiphenyl) benzo[1,2-d:5,4-d']bisoxazole; and
  - c) the reaction product of pyromellitic dianhydride and 2,2'-p-phenylene-bis(5-aminobenzoxazole).
- 25 8. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the polyimidebenzoxazole (PIBO) film at 25°C has an elastic modulus greater than 0.5 GPa.
- 30 9. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the polyimidebenzoxazole (PIBO) film at 25°C has a tensile strength greater than 250 MPa.
- 35 10. The polyimidebenzoxazole (PIBO) film of Claim 9 wherein the polyimidebenzoxazole (PIBO) has a tensile strength greater than 300 MPa at 25°C.

11. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the polyimidebenzoxazole (PIBO) film has a permanent lateral deformation of less than 0.02 percent as determined by IPC 650 2.2.4A.

5 12. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the polyimidebenzoxazole (PIBO) film has a coefficient of thermal expansion (CTE) in the XY direction between 1 and 7 ppm per °C from -55 to 125°C.

10 13. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the polyimidebenzoxazole (PIBO) polymer film has a CTE of less than 100 ppm per °C in the Z direction from -55 to 125°C.

15 14. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the polyimidebenzoxazole (PIBO) film has an elastic modulus greater than 5 GPa at 25°C.

15 15. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the electrically conductive layer is bonded directly to the PIBO film.

20 16. The polyimidebenzoxazole (PIBO) film of Claim 1 wherein the electrically conductive layer is adhered to the PIBO film by means of an adhesive.

17. The polyimidebenzoxazole (PIBO) film of Claim 1 is a panel or processed panel.

25 18. A printed wiring board having at least one dielectric layer and at least one circuitry layer wherein at least one dielectric layer is PIBO film having a tensile strength of at least 200 MPa at 25°C.

19. The printed wiring board of Claim 18 wherein the printed wiring board is a single-sided printed wiring board.

30 20. The printed wiring board of Claim 18 wherein the printed wiring board is a double-sided printed wiring board.

21. The printed wiring board of Claim 18 wherein the printed wiring board is a multilayer printed wiring board.

22. The printed wiring board of Claim 18 wherein the 35 dielectric layer is PIBO, said dielectric layer has a thickness of less than 150 microns.

23. The printed wiring board of Claim 22 wherein the dielectric layer is PIBO, said dielectric layer has a thickness of less than 50 microns.

24. The printed wiring board of Claim 18 wherein at 5 least one circuitry layer is less than 50 microns thick.

25. The printed wiring board of Claim 18 wherein at least one circuitry layer is less than 17 microns thick.

26. The printed wiring board of Claim 18 wherein at 10 least one circuitry layer is selected from the group consisting of copper, aluminum or alloys thereof.

27. The printed wiring board in Claim 18 wherein said dielectric layer has a dielectric constant between 2 and 3.3 over a frequency range of 1 KHz to 1 GHz.

28. The printed wiring board of Claim 18 wherein at 15 least one circuitry layer has at least one conductor having a line width of less than 100 microns.

29. The printed wiring board of Claim 18 wherein at least one circuitry layer has at least two conductors having a conductor spacing of less than 100 microns.

20 30. The printed wiring board of Claim 18 wherein at least two of the conductive circuitry layers have at least one interconnecting via having a diameter of less than 200 microns.

25 31. The printed wiring board of Claim 18 wherein at least one circuitry layer has at least one annular hole ring having a width between 0 (landless) and 200 microns.

32. The printed wiring board of Claim 21 wherein the multilayer printed wiring board has at least one dielectric adhesive layer, wherein the dielectric adhesive layer is an 30 adhesive or derived from an adhesive selected from the group consisting of:

- a) epoxy;
- b) polyimide;
- c) cyanate ester;
- 35 d) polyamic acid and
- e) PIBO film having an adhesive joined to at least one face.

33. The printed wiring board of Claim 18 wherein the printed wiring board passes thermal cycling test IPC 650 2.6.6B.

34. The printed wiring board of Claim 21 has a 5 circuit density of greater than 160 leads per square inch.

35. The printed wiring board of Claim 34 wherein a multichip module (MCM) has at least two surface mounted ICs.

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 96/06202A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H05K1/03

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 393 826 (HOECHST CELANESE CORP.) 24 October 1990 see page 11, line 23 - line 39; claims 11-14 ---	1,7,18
A	PATENT ABSTRACTS OF JAPAN vol. 18, no. 291 (C-1208), 3 June 1994 & JP,A,06 056992 (UNITIKA), 1 March 1994, see abstract -----	

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

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1 Date of the actual completion of the international search  16 July 1996	Date of mailing of the international search report  05.08.96
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer  Mes, L

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l. Application No

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-393826	24-10-90	US-A-	4980447	25-12-90
		CA-A-	2010772	09-09-90
		DE-D-	69026297	09-05-96
		JP-A-	3200838	02-09-91
		US-A-	5071948	10-12-91